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Quantum Mechanics of One-Dimensional Two-Particle Models. Electrons Interacting in an Infinite Square Well

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Solutions of Schrödinger's equation for the system of two particles bound in a one-dimensional infinite square well and repelling each other with a Coulomb force are obtained by the method of finite differences. For the case of a 4.0-a.u. well, the energy levels are shifted above those of the noninteracting-particle model by as much as a factor of 4 although the excitation energies are only about 50% greater. The analytical form of the solutions is also obtained and it is shown that every eigenstate is doubly degenerate due to the "pathological" nature of the one-dimensional Coulomb potential. This degeneracy is verified numerically by the finite-difference method. The properties of the model system are compared with those of the free-electron and hard-sphere models; perturbation and variational treatments are also carried out using the hard-sphere Hamiltonian as a zeroth-order approximation. The lowest several finite-difference eigenvalues converge from below with decreasing mesh size to energies below those of the "best" linear variational function consisting of hard-sphere eigenfunctions. The finite-difference solutions in general give expectation values and matrix elements more accurately than do the other approximations.

I. INTRODUCTION

One-dimensional (1-D) models are interesting and worthwhile because they are generally more mathematically tractable than their three-dimensional (3-D) analogs. Any one-dimensional problem is unquestionably a *model* in the sense that there are no physical systems to which the results apply directly, but the simplified model may yet yield some insight into the real physical system. It is clear that one must be cautious in "extrapolating" the 1-D results to three dimensions. A classic example of a valuable 1-D model is the simple free-electron model (FEM), in which the electrons move independently in a 1-D infinite square well. In spite of the relative success of this model, e.g., in its application to pi-electron spectra of conjugated molecules, a first obvious improvement is the inclusion of the 1-D Coulomb interaction among the electrons. The solution of our model gives accurate wavefunctions and energies for the two-electron case of this improved FEM and furthermore demonstrates in the general case how the "physics" may get distorted in one dimension.

In this paper we obtain, by the method of finite differences (FD), solutions of the Schrödinger equation for the system of two particles bound in an infinite square well and repelling each other with a Coulomb force.[1] The energy levels for the first few states are shifted above those of the noninteracting-particle model (FEM) by as much as a factor of 4, although the excitation energies are only 50%–70% greater. Most important, however, every state including the ground state is doubly degenerate. This is a nongroup-theoretically required degeneracy and is due to the "pathological" nature of the 1-D Coulomb potential which requires that the wavefunction vanish when the coordinates of the electrons are equal.

A central problem in the quantum theory of many-electron systems is to find approximate wavefunctions which accurately predict the properties of the system. Traditionally, one uses the variational principle to determine the "best" trial function of a given form. Often, however, this best trial function does not successfully predict other properties of the system more important to the chemist than the total energy. In order to discover directly why this "best" function fails it is necessary to examine the exact solution. For example, to study the effects of electron correlation in two-electron atoms, Kestner and Sinanoğlu[2] and Tredgold and Evans[3] independently investigated the exactly soluble 3-D model consisting of two electrons bound in a harmonic well, but repelling each other with a Coulomb force. The presence in the Hamiltonian of the attractive harmonic terms along with the Coulomb terms allowed them to separate the Schrödinger equation in the center-of-mass coordinate system. In contrast the FD method allows one to study the effects of a wide variety of attractive (nuclear) potentials on electron correlation since it does not rely on the presence of a separable potential in the Hamiltonian.

A great deal of study has been given to the problem of electronic interaction in the FEM. Several authors have investigated the effect of including explicit interelectronic interaction (Coulomb) terms in the model Hamiltonian. Araki and Araki[4] used a 2-D average over the 3-D Coulomb potential in a 1-D treatment of the cyanine dyes. In a similar manner, Huzinaga[5] re-examined the Platt model for the naphthalene molecule, including electron repulsion terms as 1-D averages over the 3-D potentials. Also, Ham and Ruedenberg[6] modified the free-electron network model by intro-

* National Science Foundation Predoctoral Fellow 1964–1967.
† Contribution No. 3434.

[1] We refer to this interacting-particle model as the IFEM, i.e., the "interacting"-free-electron model.

[2] N. Kestner and O. Sinanoğlu, Phys. Rev. **128**, 2687 (1962).

[3] R. Tredgold and J. Evans, Tech. Rept. No. 55, Physics Department, University of Maryland, 1956 (unpublished).

[4] G. Araki and H. Araki, Progr. Theoret. Phys. (Kyoto) **11**, 20 (1954).

[5] S. Huzinaga, Progr. Theoret. Phys. (Kyoto) **15**, 495 (1956).

[6] N. Ham and K. Ruedenberg, J. Chem. Phys. **25**, 1 (1956).

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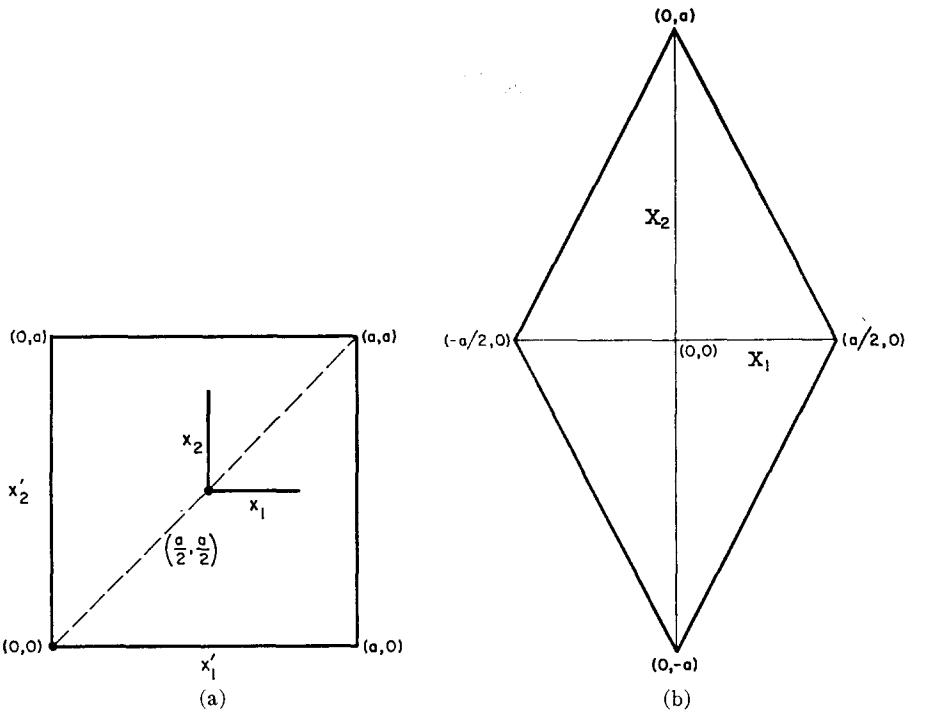

FIG. 1. Boundary conditions on the wavefunctions in various coordinate systems. (a) Coordinate systems $[x_1', x_2']$ and $[x_1, x_2]$ in which the wavefunctions vanish on the edges of a square. (b) Center-of-mass coordinate system $[X_1, X_2]$ in which wavefunctions vanish on the edges of a rhombus.

ducing the electron interaction terms as 2-D averages over the cross section of the bond path. Finally, Olszewski[7] attempted a configuration interaction treatment of linear conjugated molecules using antisymmetrized 1-D free-electron molecular orbitals (ASFEMO).[8] The solution of our model suggests several alternative methods of treating linear conjugated molecules which do not involve taking averages over arbitrary cross sections or limits of 3-D expressions.

Bolton and Scoins,[9] concerned primarily with the solution of eigenvalue problems by the finite-difference method, have reviewed attempts to solve various 2-D Schrödinger equations. Although not particularly interested in electron correlation, they obtained for the "S limit"[10] of the ground state of the helium atom a value of -2.65 a.u. (best value -2.879 a.u.).[10,11]

In the following sections we have two main purposes: to obtain accurate energies, wavefunctions, and selected properties for the model system (IFEM) discussed above and then to consider the relevance of our results to more complicated model systems. In Sec. II, the model is treated quantitatively. The analytical properties, including the "accidental" double degeneracies, are discussed in Part A; the FD method, uniqueness, and convergence properties of FD eigenfunctions, eigenvalues, and matrix elements in Part B. We also discuss numerical verification of degeneracies in Part B. Finally, in Part C we compare approximate solutions obtained by perturbation and variation methods. A discussion of the implications of our results and possible applications follows in Sec. III.

II. MATHEMATICAL TREATMENT OF THE MODEL

A. General Considerations

The time-independent Schrödinger equation for the one-dimensional system of two electrons in an infinite square well is written in atomic units in the coordinate system $[x_1', x_2']$[12]

$$H'\psi(x_1', x_2') = E\psi(x_1', x_2'), \tag{1a}$$

$$H' = -\tfrac{1}{2}[(\partial^2/\partial x_1'^2) + (\partial^2/\partial x_2'^2)] + |x_1' - x_2'|^{-1}, \tag{1b}$$

where $0 \leq x_1', x_2' \leq a$, and x_1' and x_2' denote the electron coordinates; a is the well width. Since the wavefunction must vanish outside the well, the boundary conditions on ψ in $[x_1', x_2']$ are

$$\psi(x_1', 0) \equiv 0, \quad \psi(x_1', a) \equiv 0,$$
$$\psi(0, x_2') \equiv 0, \quad \psi(a, x_2') \equiv 0. \tag{2}$$

[7] S. Olszewski, Acta Phys. Polon. **14**, 419 (1955).

[8] However, later noting that the electron repulsion integrals in his energy expression diverged, he modified the treatment by first evaluating the 3-D repulsion integrals in a cylinder and then allowing the cylinder radius to go to zero. See S. Olszewski, Acta Phys. Polon. **16**, 369 (1957).

[9] H. Bolton and H. Scoins, Proc. Cambridge Phil. Soc. **53**, 150 (1957).

[10] R. Parr, *Quantum Theory of Molecular Electronic Structure* (W. A. Benjamin, Inc., New York, 1964), p. 10.

[11] We have obtained a considerably better value for the "S limit" with little labor by employing finer meshes in setting up the FD equations. Results to be published by N. Winter, D. Diestler, and V. McKoy in this Journal.

[12] The symbol "$[\xi, \eta]$" denotes a particular coordinate system, ξ and η specifying the unit vectors for each dimension. Thus $[x_1', x_2']$ denotes the system in which the coordinates are just the distances of each electron from the origin at the left end of the well.

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These conditions require that $\psi(x_1', x_2')$ vanish on the boundary of a square of edge a [see Fig. 1(a)]. The Schrödinger equation (1a) is invariant under transformation to the system $[x_1, x_2]$, defined by

$$x_1=x_1'-a/2; \qquad x_2=x_2'-a/2.$$

However, the boundary conditions in $[x_1, x_2]$ are

$$\varphi(x_1, -a/2)\equiv 0, \qquad \varphi(x_1, a/2)\equiv 0,$$
$$\varphi(-a/2, x_2)\equiv 0, \qquad \varphi(a/2, x_2)\equiv 0. \tag{3}$$

In the center-of-mass coordinate system $[X_1, X_2]$, where

$$X_1=\tfrac{1}{2}(x_1+x_2), \qquad X_2=x_1-x_2,$$

the Schrödinger equation becomes

$$-\tfrac{1}{4}(\partial^2\Psi/\partial X_1^2)-(\partial^2\Psi/\partial X_2^2)+(\Psi/|X_2|)=E\Psi, \tag{4}$$

with the corresponding boundary conditions

$$\Psi(X_1, 2X_1+a)=0, \qquad \Psi(X_1, 2X_1-a)=0,$$
$$\Psi(X_1, -2X_1-a)=0, \qquad \Psi(X_1, -2X_1+a)=0. \tag{5}$$

These conditions specify that the wavefunction vanish on the boundary of a rhombus, the edges of which are not coincident with coordinate surfaces in $[X_1, X_2]$ [see Fig. 1(b)].

In each of the coordinate systems there is a group of operators $\mathbf{E}$, $\mathbf{i}$, $\mathbf{R}_1$, $\mathbf{R}_2$ defining coordinate transformations which leave the Hamiltonian invariant. It is simplest to define these operators in $[x_1, x_2]$, although we express them later in the other systems. Thus $\mathbf{E}$ is the identity which takes the *point* (x_1, x_2) into itself, $\mathbf{i}$ is the inversion about (0, 0) taking (x_1, x_2) into $(-x_1, -x_2)$, $\mathbf{R}_1$ is the reflection about the diagonal $x_2=x_1$ which transforms (x_1, x_2) into (x_2, x_1), and $\mathbf{R}_2$ is the reflection about the other diagonal which carries (x_1, x_2) into $(-x_2, -x_1)$. This group is isomorphic with D_2,[13] which is Abelian. Thus the group of the Schrödinger equation has only one-dimensional irreducible representations (I.R.) and hence we conclude that all the eigenstates of our system are nondegenerate, i.e., there is no *group-theoretically* required degeneracy.

Now consider the solution of the Schrödinger equation in the system $[X_1, X_2]$ by the method of separation of variables. To study the form of the components of the required solution substitute $\Psi(X_1, X_2)=\phi(X_1)\chi(X_2)$ into Eq. (4). A sum of such components will, of course, have to be used to satisfy the boundary conditions, Eq. (5). We obtain

$$\tfrac{1}{4}(d^2\phi/dX_1^2)+E_\phi\phi=0 \tag{6a}$$

and

$$-(d^2\chi/dX_2^2)+(\chi/|X_2|)-E_\chi\chi=0, \tag{6b}$$

where $E=E_\phi+E_\chi$. The *general* solution of Eq. (6a) may be written

$$\phi(X_1)=A_1\cos k_\phi X_1+A_2\sin k_\phi X_1, \tag{7}$$

where $k_\phi^2=4E_\phi$ and A_1 and A_2 are arbitrary constants. Equation (6b) is just the Coulomb wave equation for states of zero angular momentum and its *general* solution may be written

$$\chi(X_2)=X_2\exp(k_\chi X_2)\{B_1V_1(-2k_\chi X_2)+B_2V_2(-2k_\chi X_2)\}, \tag{8}$$

where V_1 and V_2 are, respectively, the regular and irregular solutions of Kummer's equation,[14] B_1 and B_2 are arbitrary constants, and $k_\chi^2=-E_\chi$. Since the irregular solution does not vanish at $X_2=0$, we can eliminate it from χ on the basis of "physical" considerations. We suppose that the exact eigenfunction Ψ contains $G_0=X_2\exp(k_\chi|X_2|)V_2$. Then the expectation value of the Hamiltonian

$$\langle\Psi|H|\Psi\rangle=\langle\Psi|K_{\rm op}|\Psi\rangle+\langle\Psi|V|\Psi\rangle,$$

where $\langle\Psi|V|\Psi\rangle$ contains a term

$$\int_{-a/2}^{+a/2} G_0^2|X_2|^{-1}\,dX_2.$$

Since G_0 is approximately constant in the neighborhood of the origin, the integrand diverges. We have

$$\int_{-a/2}^{a/2} G_0^2|X_2|^{-1}\,dX_2 \simeq \lim_{\alpha\to 0}\left\{\int_{-a/2}^{-\alpha} -X_2^{-1}\,dX_2+\int_{\alpha}^{a/2} X_2^{-1}\,dX_2\right\}$$
$$=2\lim_{\alpha\to 0}\ln(a/2\alpha).$$

Hence $\langle\Psi|V|\Psi\rangle$ diverges logarithmically and since $\langle\Psi|K_{\rm op}|\Psi\rangle>0$, we find that the eigenvalue is infinite. Hence we eliminate G_0.

The *general* solution of the relative equation (6b) may be obtained by joining the regular solutions in the two regions $X_2>0$ and $X_2<0$ to form functions of odd parity which have a continuous derivative at $X_2=0$ or functions of even parity with a cusp at $X_2=0$. Hence each state is doubly degenerate[15] and we have for the

[13] M. Tinkham, *Group Theory and Quantum Mechanics* (McGraw-Hill Book Co., New York, 1964), 1st ed., p. 327.

[14] L. Slater, *Confluent Hypergeometric Functions* (Cambridge University Press, Cambridge, England, 1960), p. 2.

[15] We note that this result may be proved rigorously by an alternative procedure. Because of the singularity in the Coulomb potential, it is not clear how the solutions for $X_2>0$ and $X_2<0$ should be joined at $X_2=0$. To ascertain the appropriate boundary conditions in the case of an infinite potential it is necessary to start with a finite potential V requiring continuity of the wavefunction and its gradient, and then take the limit as V goes to infinity (see Ref. 16). The discontinuity at $X_2=0$ in the gradient of the even wavefunctions found by this procedure is tolerable since the potential is singluar there. The same sort of discontinuities is observed in the eigenfunctions of other one-dimensional problems involving singular potentials, e.g., the particle in the box, hard spheres in a box, and the hydrogen atom (see Ref. 17).

[16] L. Schiff, *Quantum Mechanics* (McGraw-Hill Book Co., New York, 1955), 2nd ed., p. 29.

[17] R. Loudon, Am. J. Phys. **27**, 649 (1959).

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complete *general* solution of the Schrödinger equation in $[X_1, X_2]$

$$\Psi(X_1, X_2) = \mathbf{S}_j (A_{1j} \cos k_{\phi j} X_1 + A_{2j} \sin k_{\phi j} X_1) \times [\,|X_2| \exp(k_{\chi j} |X_2|) V_1(-2k_{\chi j} |X_2|)] \quad (9)$$

for the states symmetric with respect to $\mathbf{R}_1$, with a similar expression for the states antisymmetric with respect to this operation. Here $\frac{1}{4}k_{\phi j}^2 - k_{\chi j}^2 = E$, the A_{1j} and A_{2j} are arbitrary constants, and the $\mathbf{S}_j$ indicates a sum over the discrete spectrum of k and an integral over the continuum. In order to find the allowed eigenvalues and eigenfunctions we must impose the boundary conditions Eq. (5) in $[X_1, X_2]$. We have attempted to do this for the totally symmetric (A_1) states by expanding the ϕ and χ in power series and equating the coefficient of each power to zero. However, this procedure leads to an infinite set of coupled integral equations found to be highly intractable mathematically. Hence this approach has been abandoned in favor of the more generally applicable and highly tractable finite-difference method.

B. The Finite-Difference Method

In the FD method the approximate solution of the Schrödinger equation (1a) is expressed as a set of numbers ψ_i which are the approximate values of the wavefunction at a finite set of grid (mesh) points in $[x_1', x_2']$. The set of grid points is divided into *boundary* points, at which the values of ψ_i are known, and *interior* points, at which the values of ψ_i are to be determined by solving the difference equation analog of the Schrödinger equation

$$H_i\psi_i = \epsilon\psi_i, \qquad i = 1, 2, \cdots, M, \quad (10)$$

where H_i is the discretized Hamiltonian, ϵ is the discretized eigenvalue, and M is the number of *interior* points. A square mesh of size h is conveniently constructed as shown in Fig. 2(a), where the *boundary* points are denoted by circles ○ and the *interior* points by dots ●. It is not necessary to construct a mesh over the whole square since, as we have shown above, all of the exact eigenfunctions vanish along the diagonal, being either symmetric or antisymmetric with respect to $\mathbf{R}_1$. The explicit form of the difference equation analog (10) is found at each point of the mesh by expressing the partial derivatives in H in terms of Ψ_i at neighboring points. Thus we consider mesh point $i \leq M$ and denote the neighboring points as i_1, i_2, i_3, and i_4 [Fig. 2(b)]. The values ψ_{i_j} at neighboring points may be expanded in a Taylor's series as[18]

$$\psi_{i_1} = \psi_i + \left(\frac{\partial\psi}{\partial x_1'}\right)_i h + \left(\frac{\partial^2\psi}{\partial x_1'^2}\right)_i \frac{h^2}{2!} + \left(\frac{\partial^3\psi}{\partial x_1'^3}\right)_i \frac{h^3}{3!} + \left(\frac{\partial^4\psi}{\partial x_1'^4}\right)_{i,i_1} \frac{h^4}{4!},$$

$$\psi_{i_3} = \psi_i - \left(\frac{\partial\psi}{\partial x_1'}\right)_i h + \left(\frac{\partial^2\psi}{\partial x_1'^2}\right)_i \frac{h^2}{2!} - \left(\frac{\partial^3\psi}{\partial x_1'^3}\right)_i \frac{h^3}{3!} + \left(\frac{\partial^4\psi}{\partial x_1'^4}\right)_{i,i_3} \frac{h^4}{4!}.$$

Adding these equations and rearranging, we obtain

$$\left(\frac{\partial^2\psi}{\partial x_1'^2}\right)_i = \frac{\psi_{i_1} + \psi_{i_3} - 2\psi_i}{h^2} - \frac{h^2}{4!}\left[\left(\frac{\partial^4\psi}{\partial x_1'^4}\right)_{i,i_1} + \left(\frac{\partial^4\psi}{\partial x_1'^4}\right)_{i,i_3}\right].$$

A similar expression may be obtained for $(\partial^2\psi/\partial x_2'^2)_i$. For h small enough, the bracketed terms may be neglected[19] so that the difference equation analog becomes

$$\left(-4 - \frac{2h^2}{|x_{1i}' - x_{2i}'|}\right)\psi_i + \sum_{j=1}^{4} \psi_{i_j} = \lambda\psi_i, \qquad i = 1, 2, \cdots, M, \quad (11)$$

where $\epsilon = -\lambda/2h^2$. The set of equations (11) may be expressed more conveniently in matrix form

$$\mathbf{H}\psi = \lambda\psi, \quad (12)$$

where $\mathbf{H}$ is a real symmetric (Hermitian) matrix of order M, ψ is a column vector of the ψ_i, and λ is the modified eigenvalue. The structure of $\mathbf{H}$ is, of course, determined by the mesh labeling shown in Fig. 2(a). All the diagonal elements are negative and the off-diagonal elements are either 1 or 0. Since $\mathbf{H}$ is Hermitian,

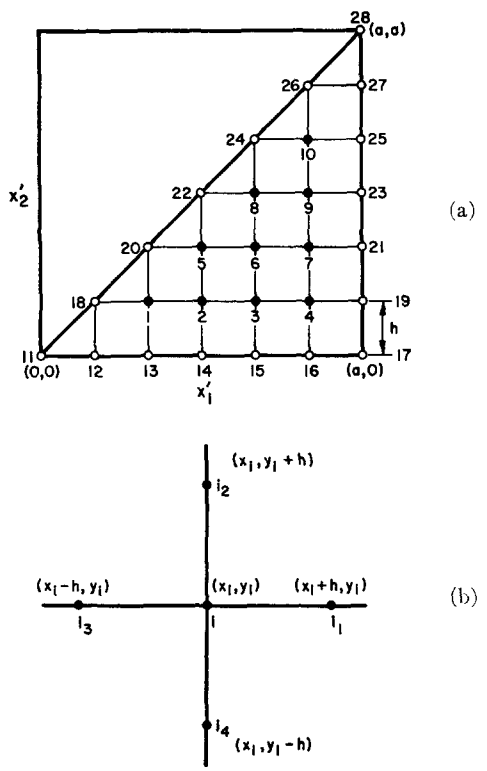

FIG. 2. Finite-difference mesh. (a) Square mesh of size $h = a/6$; a is well width. (b) Enlargement of mesh of size h around point i.

[18] See, for example, J. Todd, *Survey of Numerical Analysis* (McGraw-Hill Book Co., New York, 1962), p. 384.

[19] In a paper to be published (see Ref. 11) we show that this is a good approximation for similar mesh sizes in the He-atom "S-limit" wavefunction. There we will also include the effect of fourth-order differences by the method discussed in L. Fox, Proc. Roy. Soc. (London) **A910,** 31 (1947).

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its eigenvectors, which are approximations to the exact eigenfunctions, are orthogonal. Furthermore, the matrix $\mathbf{R}_2$, which reflects ψ across the diagonal $x_2' = -x_1' + a$, commutes with $\mathbf{H}$ so that the FD eigenvectors have the same symmetry required of the exact eigenfunctions. Thus, the eigenvectors ψ_{ws}, formed over the *whole* square by joining the discretized solutions in the two *half*-squares such that ψ_{ws} is of either even or odd parity, must transform according to the I.R.'s of D_2.

1. Uniqueness and Convergence

A symmetric $n \times n$ matrix always has n distinct (i.e., linearly independent) eigenvectors.[20] Furthermore, a Hermitian matrix can be diagonalized by a similarity transformation with a unitary matrix whose columns are the eigenvectors determined up to a phase factor.[21] Hence, we may conclude that for every mesh size h there is a set of distinct eigenvectors determined up to a constant factor, which we set by normalization.

Following the procedure of Bolton and Scoins[9] we consider whether the discretized eigenvalues, eigenfunctions, and matrix elements converge to the exact values in the limit as the mesh size h approaches zero. We assume that there exists a continuous function $\psi_c(x_1', x_2'; h)$ which satisfies the difference equation analog (11) for all values of h and that $\psi_c(x_1', x_2'; h)$ and $\lambda(h)$, the discretized eigenvalue, may be expanded as follows in the intervals $0 \leq x_1', x_2' \leq a$, $0 \leq h \leq h_0$

$$\psi_c(x_1', x_2'; h) = \sum_k \phi_k(x_1', x_2') h^k,$$

$$\lambda(h) = h^2 \sum_l c_l h^l, \tag{13}$$

or

$$\epsilon(h) = -\tfrac{1}{2} \sum_l c_l h^l,$$

where the ϕ_k may be expanded in the complete orthonormal set of exact eigenfunctions of H'. If the expansions (13) are substituted into Eq. (11), the value of ψ_c at neighboring grid points expanded in Taylor's series, and the coefficients of powers of h equated, one obtains

$$-\frac{1}{2}\left(\frac{\partial^2\phi_0}{\partial x_1'^2} + \frac{\partial^2\phi_0}{\partial x_2'^2}\right) + \frac{\phi_0}{|x_1' - x_2'|} = -\tfrac{1}{2} c_0 \phi_0, \tag{14a}$$

$$-\frac{1}{2}\left(\frac{\partial^2\phi_1}{\partial x_1'^2} + \frac{\partial^2\phi_1}{\partial x_2'^2}\right) + \frac{\phi_1}{|x_1' - x_2'|} = -\tfrac{1}{2}(c_0\phi_1 + c_1\phi_0), \tag{14b}$$

$$-\frac{1}{2}\left(\frac{\partial^2\phi_2}{\partial x_1'^2} + \frac{\partial^2\phi_2}{\partial x_2'^2}\right) - \frac{1}{24}\left(\frac{\partial^4\phi_0}{\partial x_1'^4} + \frac{\partial^4\phi_0}{\partial x_2'^4}\right) + \frac{\phi_2}{|x_1' - x_2'|} = -\tfrac{1}{2}(c_0\phi_2 + c_1\phi_1 + c_2\phi_0). \tag{14c}$$

Since Eq. (14a) is just the Schrödinger equation, we see that ϕ_0 is the exact eigenfunction and $E = -c_0/2$ the exact eigenvalue. Multiplying Eq. (14b) by ϕ_0 and integrating over the range $0 \leq x_1', x_2' \leq a$, we obtain

$$\int_0^a \int_0^a \phi_0 H' \phi_1 dx_1' dx_2' = E \int_0^a \int_0^a \phi_0 \phi_1 dx_1' dx_2' - \tfrac{1}{2} c_1 \int_0^a \int_0^a \phi_0^2 dx_1' dx_2'. \tag{15}$$

Since H' is Hermitian and the ϕ_k real, the left member of Eq. (15) equals the first term of the right member and

$$-\tfrac{1}{2} c_1 \int_0^a \int_0^a \phi_0^2 dx_1' dx_2' = 0.$$

Hence $c_1 = 0$. Thus from Eq. (14b) $\phi_1 \equiv 0$ or is a multiple of ϕ_0. We set $\phi_1 \equiv 0$, thus obtaining $c_3 = 0$ in a manner similar to that above. If we multiply Eq. (14c) by ϕ_0 and integrate as before, we obtain eventually

$$c_2 = -\frac{1}{12} \int_0^a \int_0^a \phi_0 \left(\frac{\partial^4}{\partial x_1'^4} + \frac{\partial^4}{\partial x_2'^4}\right) \phi_0 dx_1' dx_2'.$$

Thus we see that the error in the leading term of the discretized energy $\epsilon(h)$ is of order h^2:

$$\epsilon(h) = E + c_2 h^2 + c_4 h^4 + \cdots.$$

It can be shown that, under rather general conditions, as h tends to zero, the solutions of the difference equation approach the solution of the differential equation, i.e., the discretization error usually decreases as the mesh size is reduced. A small value of h will minimize the truncation error inherent in Eq. (11) but will increase the size of the matrix to be diagonalized. Although the eigenvalues of fairly large matrices of this type can be obtained quite accurately and economically,[11] it would be advantageous to avoid such large matrices. Since the difference between the eigenvalue at a given mesh size and the exact eigenvalue is a polynomial in h^2, one may use the Richardson extrapolation technique[22]: Put a polynomial through the values obtained at various "not too large" mesh sizes and extrapolate to "zero" mesh size. Of course, this extrapolation process may be somewhat dangerous since it is necessary to employ mesh sizes sufficiently small to be certain that the extrapolant lies close to the true eigenvalue. Exactly how small a mesh size is required must be ascertained by investigation of specific cases. As we show below, there are several cogent reasons why our solutions should be reliable, e.g., agreement with variation and perturbation treatments, small differences between FD eigenvectors for mesh sizes differing by a factor of 2, and results obtained for the "S limit" of the He atom using much smaller mesh sizes and including fourth-difference terms in the discretized Schrödinger equation.

Consider the matrix element of an operator $\hat{M}$ con-

[20] L. Fox, *An Introduction to Numerical Linear Algebra* (Clarendon Press, Oxford, England, 1964), p. 42.

[21] E. Wigner, *Group Theory* (Academic Press Inc., New York, 1959), p. 26.

[22] L. Richardson and J. Gaunt, Trans. Roy. Soc. (London) **A226**, 299 (1927).

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necting states k and l. We write

$$\langle k \mid \hat{M} \mid l\rangle \simeq \langle \psi_{ck}(x_1', x_2'; h) \mid \hat{M} \mid \psi_{cl}(x_1', x_2'; h)\rangle = \int_0^a \int_0^a \psi_{ck}(x_1', x_2'; h)\hat{M}\psi_{cl}(x_1', x_2'; h)\,dx_1'dx_2'. \tag{16a}$$

Substituting the expansion of Eq. (13) for $\psi_c(x_1', x_2'; h)$, we obtain

$$\begin{aligned}\langle \psi_{ck} \mid \hat{M} \mid \psi_{cl}\rangle &= \langle \sum_r \phi_{l,}h^r \mid \hat{M} \mid \sum_p \phi_{k,p}h^p\rangle \\ &= \sum_r h^r\Big(\sum_{p=0}^{r} \langle \phi_{l,} \mid \hat{M} \mid \phi_{k,r-p}\rangle\Big) \\ &= \langle \phi_{l0} \mid \hat{M} \mid \phi_{k0}\rangle + (\langle \phi_{l0} \mid \hat{M} \mid \phi_{k1}\rangle \\ &\quad + \langle \phi_{l1} \mid \hat{M} \mid \phi_{k0}\rangle)h + (\langle \phi_{l0} \mid \hat{M} \mid \phi_{k2}\rangle \\ &\quad + \langle \phi_{l1} \mid \hat{M} \mid \phi_{l2}\rangle + \langle \phi_{l2} \mid \hat{M} \mid \phi_{k0}\rangle)h^2 \\ &\quad + O(h^3) \\ &= \langle k \mid \hat{M} \mid l\rangle + O(h^2).\end{aligned} \tag{16b}$$

Hence as h approaches zero, the discretized matrix element approaches the exact value with error of order h^2, since $\phi_{j1} \equiv 0$, for all j.

2. Method of Solution of the Finite-Difference Equations

In order for the set of homogeneous equations (11) to have a nontrivial solution, the determinantal equation

$$|\mathbf{H} - \lambda \mathbf{I}| = 0$$

must hold, where $\mathbf{I}$ is the $M \times M$ unit matrix. The eigenvalues λ are determined by solving this Mth-degree equation. For large *mesh* sizes ($M \leq 4$), the roots may be found analytically. For $M > 4$ the problem is solved by diagonalization of $\mathbf{H}$ by the Householder method on a computer. Symmetry serves as a useful check on the accuracy of eigenvectors for a given mesh size. Various approximations, $\epsilon_n(h) = -(1/2h^2)[\lambda_n(h)]$, to a particular eigenvalue E_n are obtained for a series of values of h corresponding to $M = 10$, 15, 21, 28, 36, 45, 55, 66, and 78. To obtain an accurate estimate of the true eigenvalue E_n for a given state, we extrapolate to zero mesh size using the method of Richardson and Gaunt[22] as discussed above, which depends on the fact that the discretized eigenvalue is expressible as a series in even powers of h.

Matrix elements of operators $\hat{M}(x_1', x_2')$, e.g., expectation values and transition moments, are approximated for a given mesh size h by

$$\langle i \mid \hat{M} \mid j\rangle \simeq \sum_{k=1}^{M(h)} \psi_{ik}M_k(x_{1k}', x_{2k}')\psi_{jk}, \tag{17}$$

where i and j denote the eigenstates connected by $\hat{M}$, $M_k(x_{1k}', x_{2k}')$ is the FD analog of the operator M at point k of the mesh; ψ's now have two subscripts, the first indicating the eigenstate and the second the mesh point. ψ_k's are normalized so that

$$\sum_{k=1}^{M} \psi_{ik}^2 = 1.$$

Of course, the matrix elements may be evaluated by more accurate numerical quadrature methods.[23] In a few cases examined these methods yielded values very little different from those calculated from the simpler expression Eq. (17). We note that if one wishes to compare eigenvectors corresponding to different mesh sizes, it is necessary to normalize the approximate eigenfunction over the half-square $x_1' \geq x_2'$. We do this below.

3. Results

Results of calculations performed for the case of a square well of width 4.00 a.u. are shown in Table I.

The eigenvectors corresponding to the eigenvalues ϵ_1, ϵ_2, etc. are, of course, approximations to the exact eigenfunctions ψ_{1ex}, ψ_{2ex}, etc., in the *half*-square $x_1' > x_2'$. Since the exact eigenstates are all doubly degenerate, we form the FD approximations over the *whole* square by joining the reflection of ψ (or $-\psi$) in the *half*-square $x_1' < x_2'$ with ψ in the *half*-square $x_1' > x_2'$. Thus we have doubly degenerate eigenstates whose approximate eigenfunctions are either symmetric or antisymmetric with respect to R_1 and transform according to the I.R.'s of D_2. The symmetric states are denoted by a superscript $+$ and the antisymmetric states by $-$. Figure 3 shows probability amplitude contours (obtained by linear interpolation) for $h = 0.50$ for the first three symmetric eigenstates of the 4.00-a.u. well. A three-dimensional plot of the approximate symmetric FD ground-state eigenfunction is shown in Fig. 4. An indication of the relative accuracy of eigenvectors corresponding to different mesh sizes may be obtained by comparing eigenvectors generated from meshes whose sizes differ by a factor of 2, such that each point of the coarser mesh coincides with alternate points of the finer mesh. Such a comparison is made in Table II for the ground- and first excited-state eigenvectors (normalized over the *half*-square) and shows that the eigenfunction changes very little when the mesh size is halved. This is a commonly used method[18] of estimating the accuracy of a finite-difference solution. Usually if the difference between two solutions with quite different mesh sizes is small, one may feel justified in assuming that the error is small. Our results certainly indicate this.

In $[x_1, x_2]$ the matrix elements of $\mathbf{x} = x_1\mathbf{e}_1 + x_2\mathbf{e}_2$, where $\mathbf{e}_1$ and $\mathbf{e}_2$ are unit vectors, may be written

$$\langle i \mid \mathbf{x} \mid j\rangle_{ws} = \langle i \mid x_1 \mid j\rangle_{ws}\mathbf{e}_1 + \langle i \mid x_2 \mid j\rangle_{ws}\mathbf{e}_2, \tag{18}$$

where the subscript ws denotes that the integral is over the *whole* square. Each of these integrals may be broken

[23] M. Abramowitz and I. Stegun, *Handbook of Mathematical Functions* (Natl. Bur. Std. Appl. Math. Ser. 55, 1964).

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TABLE I. Properties (in atomic units) as a function of mesh size for a well width of 4.00 a.u.

Property	Mesh size 0.666	0.571	0.500	0.444	0.400	0.363	0.333	0.300	0.287	Extrapolated values
ϵ_1	2.15726	2.19336	2.21718	2.23369	2.24558	2.25442	2.26118	2.26645	2.27064	2.28_1
ϵ_2	3.44520	3.59209	3.69108	3.76054	3.81102	3.84881	3.87779	3.90049	3.91859	3.96_4
ϵ_3	4.16623	4.34877	4.46940	4.55340	4.61417	4.65953	4.69426	4.72143	4.74307	4.79_7
$\langle 1^+ \mid x_1' \mid 1^+\rangle$	1.999	1.999	1.999	1.999	1.999	1.999	1.999	1.999	1.999	1.99_9
$\mid \langle 1^+ \mid x_1' \mid 2^+\rangle \mid$	0.359	0.362	0.363	0.364	0.364	0.364	0.364	0.364	0.364	0.36_4
$\mid \langle 1^+ \mid x_1' \mid 3^+\rangle \mid$	5.0×10^{-8}	9.0×10^{-8}	1.0×10^{-8}	4.5×10^{-8}	9.5×10^{-8}	15.0×10^{-8}	5.0×10^{-8}	15.0×10^{-8}	41.0×10^{-8}	...
$\langle 2^+ \mid x_1' \mid 2^+\rangle$	1.999	1.999	1.999	1.999	1.999	1.999	1.999	1.999	1.999	1.99_9
$\mid \langle 2^+ \mid x_1' \mid 3^+\rangle \mid$	0.277	0.304	0.316	0.322	0.326	0.329	0.331	0.332	0.333	0.33_5
$\langle 3^+ \mid x_1' \mid 3^+\rangle$	1.999	1.999	1.999	1.999	1.999	1.999	1.999	1.999	1.999	1.99_9
$\langle 1^+ \mid x_1'^2+x_2'^2 \mid 1^+\rangle$	9.859	9.864	9.864	9.863	9.862	9.861	9.860	9.859	9.858	9.86
$\langle 2^+ \mid x_1'^2+x_2'^2 \mid 2^+\rangle$	9.809	9.844	9.851	9.853	9.852	9.851	9.850	9.849	9.848	9.85
$\langle 3^+ \mid x_1'^2+x_2'^2 \mid 3^+\rangle$	10.324	10.375	10.391	10.396	10.398	10.399	10.399	10.399	10.399	10.40
$\langle 1^+ \mid V \mid 1^+\rangle$	0.6846	0.6904	0.6942	0.6969	...	...	...	...	...	0.700_6
$\langle 2^+ \mid V \mid 2^+\rangle$	0.8337	0.8489	0.8593	0.8665	...	...	...	...	...	0.876_1
$\langle 3^+ \mid V \mid 3^+\rangle$	0.7581	0.7810	0.7948	0.8039	...	...	...	...	...	0.816_1

up into two integrals, one over the *lower half*-square (lhs) where $x_1>x_2$ and one over the *upper half*-square (uhs). Thus

$$\langle i \mid x_1 \mid j\rangle_{\text{ws}}=\langle i \mid x_1 \mid j\rangle_{\text{lhs}}+\langle i \mid x_1 \mid j\rangle_{\text{uhs}}. \quad (19)$$

Now if both ψ_i and ψ_j are either symmetric or antisymmetric, $\psi_i\psi_j$ is symmetric about $x_1=x_2$, whereas if only one is antisymmetric $\psi_i\psi_j$ is antisymmetric. Further, since x_1 in uhs at (x_2, x_1) is equal to x_2 in lhs at the reflected point (x_1, x_2), we can rewrite Eq. (19) as

$$\langle i \mid x_1 \mid j\rangle_{\text{ws}}=\langle i \mid x_1\pm x_2 \mid j\rangle_{\text{lhs}}=\langle i \mid \pm x_2+x_1 \mid j\rangle_{\text{uhs}}, \quad (20)$$

where the + sign holds if both i and j are symmetric or antisymmetric and the − if only one is antisymmetric. From Eq. (20) we deduce

$$\langle i \mid x_1 \mid j\rangle_{\text{ws}}=\tfrac{1}{2}\langle i \mid x_1\pm x_2 \mid j\rangle_{\text{ws}}. \quad (21a)$$

In a similar manner,

$$\langle i \mid x_2 \mid j\rangle_{\text{ws}}=\tfrac{1}{2}\langle i \mid x_2\pm x_1 \mid j\rangle_{\text{ws}} \quad (21b)$$

with the same sign convention. If ψ_i and ψ_j transform according to the same IR, then $\psi_i\cdot\psi_j$ transforms totally symmetrically (A_1). Then, since (x_1+x_2) transforms as B_2, the total integrand transforms as B_2. We conclude that $\langle i \mid x_1 \mid j\rangle=0$ in $[x_1, x_2]$ or 2.0 in $[x_1', x_2']$. Table I confirms these group-theoretical results. Furthermore, since $x_1^2+x_2^2$ and $V=1/\mid x_1-x_2 \mid$ both transform according to A_1, their expectation values do not vanish in general. However, all matrix elements of these operators connecting eigenstates of different symmetry must vanish.

Ground-state energies, extrapolated by Richardson's method from mesh sizes corresponding to $M=10$, 15, 21, and 28, are plotted as a function of well width in Fig. 5. In particular we verify that the FD eigenfunctions satisfy the virial theorem approximately. For any system of particles interacting by Coulomb potentials the virial theorem is given by

$$2\langle K_{\text{op}}\rangle_{\eta=a}+\langle V\rangle_{\eta=a}=2E_a-\langle V\rangle_{\eta=a}=-a(\partial E/\partial\eta)_{\eta=a}, \quad (22)$$

where E_a is the total energy, η is a scale factor, in our case the well width, and a is a particular value of η.[24] The quantity $a(\partial E/\partial\eta)_{\eta=a}$, calculated using values of $(\partial E/\partial\eta)$ obtained by five-point interpolation,[23] is tabulated in Table III along with $2E_a-\langle V\rangle_{\eta=a}$. The increasing percentage error with well width is due to the fact that extrapolations for larger well widths are approximately as inaccurate as for smaller, yet the virial is decreasing with increasing well width.

4. *Numerical Verification of Degeneracy*

When the boundary condition along the diagonal $x_1'=x_2'$ is relaxed and a rectangular mesh with $n(n+1)$ *interior* points (arranged $n+1$ horizontal by n vertical)

[24] See, for example, P.-O. Löwdin, J. Mol. Spectry. **3**, 46 (1959).

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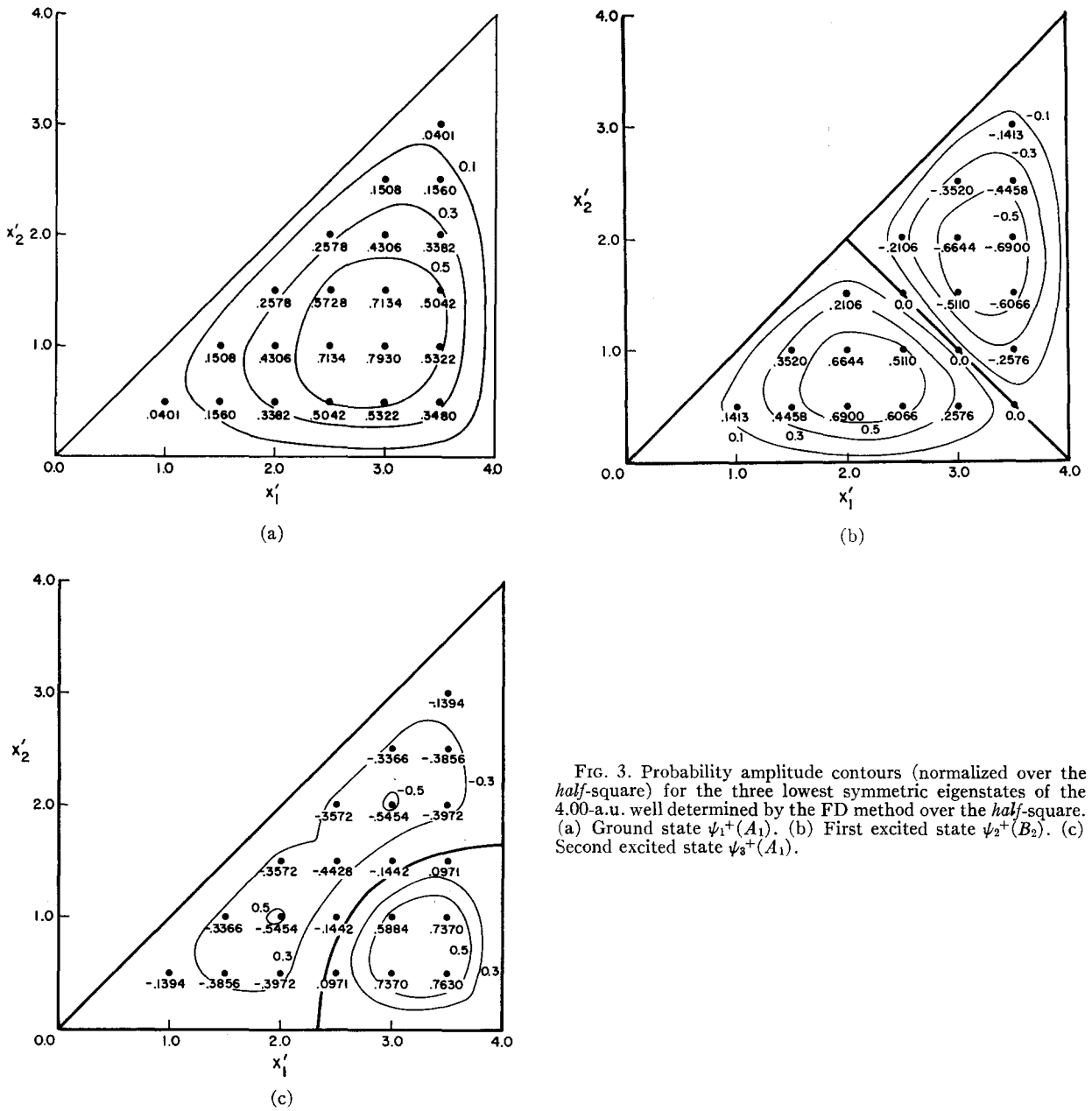

FIG. 3. Probability amplitude contours (normalized over the *half*-square) for the three lowest symmetric eigenstates of the 4.00-a.u. well determined by the FD method over the *half*-square. (a) Ground state $\psi_1^+(A_1)$. (b) First excited state $\psi_2^+(B_2)$. (c) Second excited state $\psi_3^+(A_1)$.

constructed over the *whole* square such that no mesh point lies on the diagonal, near degeneracies occur in pairs, the eigenvector associated with the lesser of the two eigenvalues (see Table IV) being symmetric with respect to $\mathbf{R}_1$ and that associated with the greater being antisymmetric. The eigenvalues of the lowest four eigenstates (two lowest nearly degenerate pairs) of the 4.00-a.u. well are listed in Table IV as a function of n along with the Richardson extrapolants. We note that the eigenvalue for the lower state of the 1–2 pair converges less rapidly than the eigenvalue of the higher state, thus indicating that in the limit $n=\infty$ exact degeneracy would occur. We also note that the upper-state eigenvalue of neither pair is greater than the corresponding eigenvalue obtained from the *half*-square treatment. Probability amplitude contours (normalized over the *whole*-square) for the lowest nearly degenerate pair are pictured in Fig. 6. The heavy dark lines represent the approximate nodes. Note that the inversion **i** is the only operator transforming mesh points in lhs into mesh points in uhs, although the contours indicate that the other required symmetry is present.

C. Comparison of Results with Other Approximate Treatments

In order to compare the accuracy of the approximate eigenvalues and functions found by the FD method and also to assess the effects of interelectronic inter-

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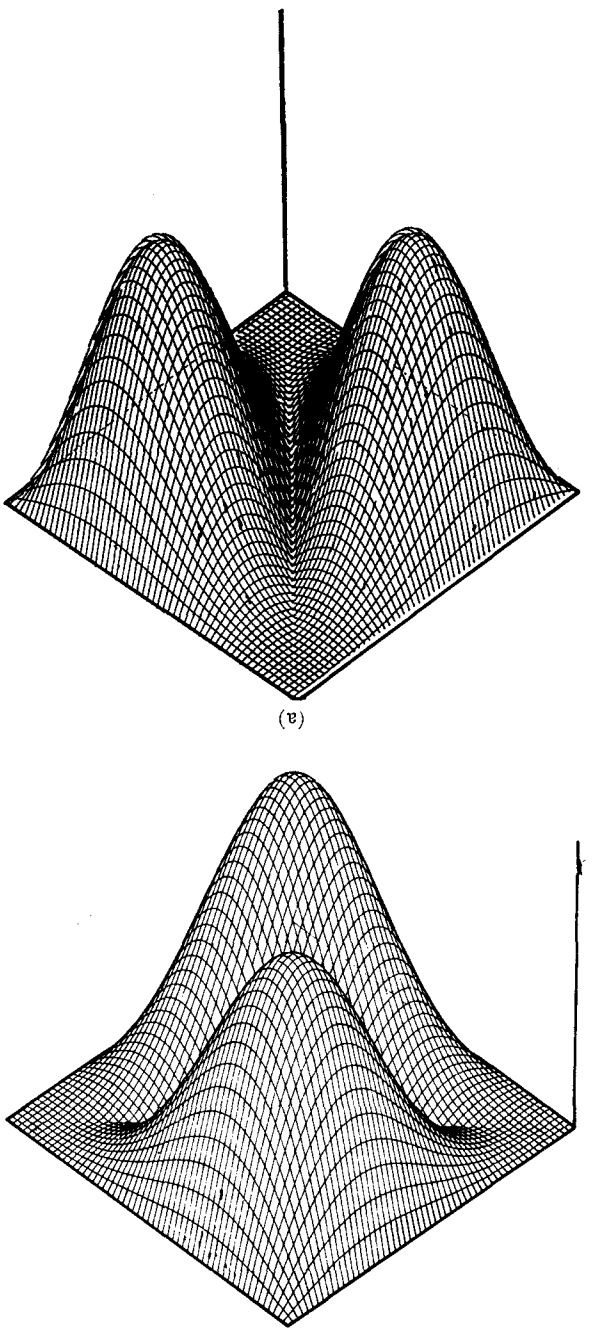

(a)

(b)

FIG. 4. Three-dimensional plots of symmetric FD ground-state eigenvector for the 4.00-a.u. well (interpolated from $M=78$). θ and ϕ have the usual significance as spherical polar coordinates. Viewing angle: (a) $\theta=45°$; $\phi=45°$; (b) $\theta=45°$, $\phi=135°$.

action on the properties of the system, it is advantageous to consider some other perhaps less accurate approximations.

1. FEM

As a zeroth-order approximation we neglect the electronic interaction entirely. The Hamiltonian for the model system becomes simply that of two independent particles in an infinite square well, whose eigenvalues and associated eigenfunctions may be written in $[x_1', x_2']$:

$$\phi_{\mathrm{FEM}}(n, m; x_1', x_2') = \frac{2}{a}\left(\sin\frac{n\pi x_1'}{a}\sin\frac{m\pi x_2'}{a} \pm \sin\frac{m\pi x_1'}{a}\sin\frac{n\pi x_2'}{a}\right)$$

$$E_{\mathrm{FEM}}(n, m) = (\pi^2/2a^2)(n^2+m^2), \tag{23}$$

where the + and − signs hold when $n\neq m$. If one attempts to improve the FEM approximation by using the FEM Hamiltonian as an unperturbed Hamiltonian and including the 1-D Coulomb interaction as a perturbation, one finds that the integrals involved in the first-order corrections to the energies and wavefunctions diverge, since the integrand in $\int\psi_0^* H'\psi_0 d\tau$ behaves as $1/|x_1'-x_2'|$ in the region of $x_1'=x_2'$. This suggests that we do perturbation theory on a system whose wavefunctions are required to vanish on $x_1'=x_2'$, i.e., a system in which a large part of interelectronic interaction has been accounted for. Such a system is that of two-point hard spheres (HSM) in an infinite square well.

2. HSM

The HSM Hamiltonian is identical to the FEM Hamiltonian, except that the hard-sphere condition requires that the wavefunctions vanish on $x_1'=x_2'$, where the potential becomes infinite. Because of the singularity in the potential, every state is at least doubly degenerate (for the reasons discussed above in Part A). Further degeneracies occur for states $\phi_{\mathrm{HSM}}(n, m)$ and $\phi_{\mathrm{HSM}}(n', m')$ for which $n^2+m^2=n'^2+m'^2$. These degeneracies are all "accidental" in the sense that they are not group-theoretically required. Thus the energy levels and wavefunctions (normalized

TABLE II. Comparison of FD ground- and first-excited-state eigenvectors for the 4.00-a.u. well.

State	Ground state		First excited state	
Mesh size	0.571	0.286	0.571	0.286
Mesh point				
1	0.03821	0.03751	0.12456	0.12663
2	0.14178	0.14177	0.34840	0.35116
3	0.27866	0.27775	0.42171	0.41246
4	0.34600	0.34196	0.21740	0.21612
5	0.24750	0.24260	0.0	0.0
6	0.12818	0.13129	0.22911	0.24444
7	0.33380	0.33811	0.29243	0.29746
8	0.46116	0.46084	0.0	0.0
9	0.34602	0.34196	−0.21740	−0.20612
10	0.17995	0.18162	0.0	0.0
11	0.33380	0.33810	−0.29243	−0.29746
12	0.27866	0.27775	−0.42171	−0.41246
13	0.12818	0.13129	−0.22911	−0.24444
14	0.14178	0.14177	−0.34840	−0.35116
15	0.03821	0.03751	−0.12456	−0.12663

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over the *half*-square) are

$$E_{\mathrm{HSM}}(n,m)=(\pi^2/2a^2)(n^2+m^2), \tag{24a}$$

$$\phi^{+}_{\mathrm{HSM}>}(n,m;x_1',x_2')=\frac{2}{a}\left(\sin\frac{n\pi x_1'}{a}\sin\frac{m\pi x_2'}{a}-\sin\frac{m\pi x_1'}{a}\sin\frac{n\pi x_2'}{a}\right); \qquad x_1'>x_2', \tag{24b}$$

$$\phi^{+}_{\mathrm{HSM}<}(n,m;x_1',x_2')=\frac{-2}{a}\left(\sin\frac{n\pi x_1'}{a}\sin\frac{m\pi x_2'}{a}-\sin\frac{m\pi x_1'}{a}\sin\frac{n\pi x_2'}{a}\right); \qquad x_1'<x_2', \tag{24c}$$

$$\phi^{-}_{\mathrm{HSM}}(n,m;x_1',x_2')=\frac{2}{a}\left(\sin\frac{n\pi x_1'}{a}\sin\frac{m\pi x_2'}{a}-\sin\frac{m\pi x_1'}{a}\sin\frac{n\pi x_2'}{a}\right), \tag{24d}$$

all x_1' and x_2', where $n\neq m$. From Expressions (24) it is clear that

$$\phi^{+}_{\mathrm{HSM}}(n,m;x_1',x_2')=\phi^{+}_{\mathrm{HSM}}(n,m;x_2',x_1')$$

and

$$\phi^{-}_{\mathrm{HSM}}(n,m;x_1',x_2')=-\phi^{-}_{\mathrm{HSM}}(n,m;x_2',x_1').$$

Using the HSM Hamiltonian as an unperturbed Hamiltonian, we calculate corrections to first- and second-order in the energies and to first-order in the wavefunctions for the first two symmetric eigenstates of the 4.00-a.u. well (see Tables V and VI). The first- and second-order corrections to the energy are given by the expressions

$$E_{nm}^{(1)}=\langle\phi^{+}_{\mathrm{HSM}}(n,m)\mid(1/|x_1'-x_2'|)\mid\phi^{+}_{\mathrm{HSM}}(n,m)\rangle, \tag{25a}$$

$$E_{nm}^{(2)}=\sum_{l}\sum_{k>l}{}'\,\langle\phi^{+}_{\mathrm{HSM}}(n,m)\mid(1/|x_1'-x_2'|)\mid\phi^{+}_{\mathrm{HSM}}(l,k)\rangle\langle\phi^{+}_{\mathrm{HSM}}(l,k)\mid(1/|x_1'-x_2'|)\mid\phi^{+}_{\mathrm{HSM}}(n,m)\rangle \times[E_{\mathrm{HSM}}(n,m)-E_{\mathrm{HSM}}(l,k)]^{-1}. \tag{25b}$$

Although these integrals may be evaluated analytically (see Appendix), for the purposes of the present calculation they were done numerically by a Simpson's rule routine on a computer. The numerical and analytical results for selected integrals agree closely, as demonstrated by the small errors in integrals which vanish by group theory (see Table VI). The energies corrected to second-order in Table V were calculated including the first ten terms of the sum (25b); matrix elements were evaluated from the first-order wavefunctions given by

$$\psi_{nm}=\phi^{+}_{\mathrm{HSM}}(n,m)+\sum_{l=1}^{N-1}\sum_{k>l}^{N}[E_{\mathrm{HSM}}(n,m)-E_{\mathrm{HSM}}(l,k)]^{-1}\,\langle\phi^{+}_{\mathrm{HSM}}(l,k)\left|\frac{1}{|x_1'-x_2'|}\right|\phi^{+}_{\mathrm{HSM}}(n,m)\rangle\phi^{+}_{\mathrm{HSM}}(l,k), \tag{26}$$

where $N=5$. Properties involving the third eigenstate were not included since this state is of the same symmetry as the ground state.

We note that the double degeneracies due to the singularity in the hard-sphere potential are not split since the perturbation operator $1/|x_1'-x_2'|$ does not connect symmetric and antisymmetric states.

The Ritz linear variation treatment employing an expansion in N HSM eigenfunctions is also carried out for the 4.00 a.u. well. We express the variational function as

$$\phi_v=\sum_{nm}c_{nm}\phi^{+}_{\mathrm{HSM}}(n,m;x_1',x_2').$$

Since the ϕ^{+}_{HSM} form a complete orthonormal set, the requirement that $\langle\phi_v\mid H'\mid\phi_v\rangle$ be stationary for first-order variations in the c_{nm} leads to the equations

$$\sum_{n=1}^{m-1}\sum_{m>n}^{N}c_{nm}\{\langle\phi^{+}_{\mathrm{HSM}}(n,m)\mid H'\mid\phi^{+}_{\mathrm{HSM}}(k,l)\rangle-\epsilon\delta_{nk}\delta_{ml}\}=0, \qquad k=1,2,\cdots,l-1;\ l>k.$$

To find the eigenvalues ϵ, which are approximations to the true eigenvalues, we have diagonalized the H' matrix by the Householder method on a computer. This is done for $N=1$, 2, and 5 and the results are collected in Tables V and VI. The energy $\langle\phi_{v1}\mid H'\mid\phi_{v1}\rangle$ for the variational function

$$\phi_{v1}=x_1'(x_1'-a)x_2'(x_2'-a)(x_1'-x_2')$$

is also included in Table V for comparison.

In order to compare the wavefunctions calculated by these various approximations, we expand the FD eigenfunctions in the complete orthonormal set of HSM eigenfunctions. The expansion coefficients for the ground-state eigenfunction are listed in Table VI along with those of the HSM and the HSM perturbation and variational treatments. All of the wavefunctions are normalized over the *half*-square in $[x_1', x_2']$. We also compare some average properties predicted by these

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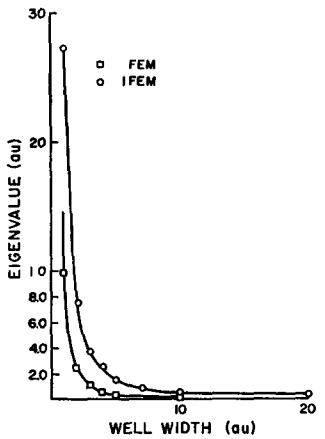

FIG. 5. Ground-state eigenvalue as a function of well width for two electrons with (a) no interaction (FEM) (b) one-dimensional Coulomb potential (IFEM).

various approximations in Table V. All matrix elements and expectation values are calculated for the states symmetric with respect to $\mathbf{R}_1$.

From Table V we note that no variational function gives an energy less than the ground-state FD eigenvalue. Furthermore, the "best" trial function, the 10-term HSM function, yields an energy about 0.5% above that of the extrapolated FD eigenvalue for the ground state. We conclude that the FD method is converging to the exact eigenvalue from below and gives a very good lower bound to the true eigenvalue. The energies determined by first-order perturbation theory on the HSM are very inaccurate, in general. It is clear that the first-order corrections to the energy are not small and hence we should not be surprised that first-order theory is inaccurate in this instance. However, the second-order corrections lower the energies nearly to those of the variational values, and higher-order corrections appear to be progressively less important. We note further that since the unperturbed energy is proportional to $1/a^2$ and the first-order correction to $1/a$, we would expect the accuracy of the first-order treatment to improve for smaller well widths.

Table VI indicates that, for the coefficients that do not vanish by group theory, i.e., c_{12}, c_{14}, c_{23}, c_{25}, and c_{34}, the 10-term HSM variational ground-state function agrees remarkably well with the $M=78$ $(h=0.285)$ FD eigenfunction; matrix elements are also in close agreement. The HSM ground-state eigenfunction corrected to first order by perturbation theory also agrees well with the FD treatment, although matrix elements do not compare as favorably.

TABLE III. Verification of virial theorem for the IFEM.

Well width a	$(2E_a-\langle V\rangle_{\eta=a})$	$-a(\partial E/\partial\eta)_{\eta=a}$	% Error[a]
3.00	6.42	6.72	4.5
4.00	3.82	3.56	7.3
5.00	2.55	2.90	12.1

[a] Based on $a(\partial E/\partial\eta)_{\eta=a}$. See Eq. (22).

TABLE IV. Eigenvalues of the lowest four eigenstates for the 4.00-a.u. well obtained by the FD treatment over the *whole* square.

Eigenstate n	1	2	3	4
6	2.03624	2.21361	3.37296	3.65420
7	2.06110	2.23207	3.44395	3.73663
8	2.08029	2.24502	3.49775	3.79488
9	2.09554	2.25446	3.53989	3.83759
10	2.10795	2.26154	3.57379	3.86983
11	2.11824	2.26699	3.60162	3.89476
Extrapolated	2.18	2.28	3.76	3.96

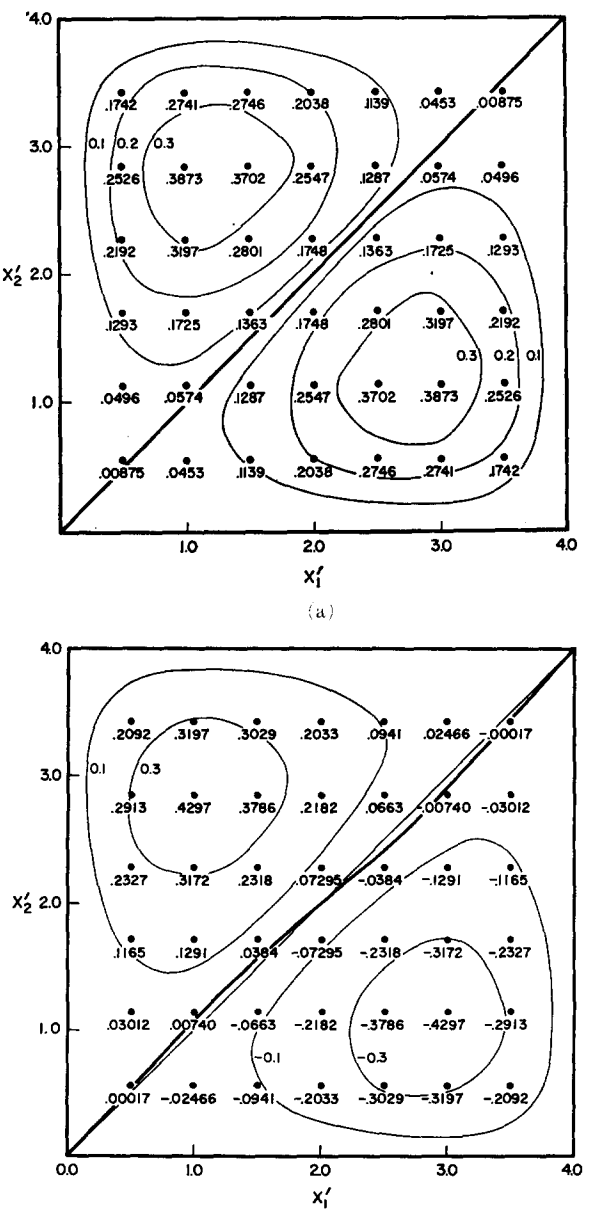

FIG. 6. Probability amplitude contours (normalized over the *whole* square) for the lowest pair of nearly degenerate states of the 4.00-a.u. well. (a) Ground state (symmetric). (b) First excited state (antisymmetric).

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TABLE V. Comparison of FD results with other approximate treatments of the 4.00-a.u. well.

Approximation	Eigenstate	Eigenvalue	Matrix element $\langle i \mid x_1' \mid 1 \rangle$	Matrix element $\langle i \mid x_1' \mid 2 \rangle$	Matrix element $\langle i \mid x_1' \mid 3 \rangle$	Expectation value of $x_1'^2+x_2'^2$
Finite difference (FD) (extrapolated to $h=0$)	1	2.281	1.999	0.364	$4.\times10^{-7}$ [b]	9.86
	2	3.964		1.999	0.335	9.85
	3	4.798			1.999	10.40
Free-electron model (FEM)	1	0.61684	2.000	0.00	0.0	8.90
	2	1.5421		2.000	0.0	10.16
	3	2.4674			2.00	10.26
Hard-sphere model (HSM)	1	1.5421	2.000	0.389	$3.\times10^{-5}$ [b]	9.65
	2	3.0842		2.000	0.397	9.77
	3	4.0095			2.000	9.81
HSM perturbation treatment	1	2.291	2.043	0.368	...	10.08
	2	4.036		2.034	...	10.01
	3	...			...	...
HSM variational treatment						
(a) 1 function ($n=1$, $m=2$)	1	2.353	2.000	...	...	9.65
(b) 2 functions ($n=1$, $m=2$; $n=1$, $m=3$)	1	2.353[a]	...	...	...	...
	2	4.097	...	...	...	...
(c) 10 functions ($n=1$, $m=2,\cdots$, 5; $n=2$, $m=3$, $\cdots$, 5; $n=3$, $m=4$, 5; $n=4$, $m=5$)	1	2.298	2.000	0.364	$3.\times10^{-4}$ [b]	9.85
	2	4.040	...	2.000	0.336	9.84$_9$
	3	4.887	...	...	2.000	10.40
Variational function $x_1'(x_1'-a)x_2'(x_2'-a)(x_1'-x_2')$	1	2.382	...	...	...	...

[a] These values are identical with energies corrected to first order.

[b] These elements vanish by group theory.

III. DISCUSSION

The accidental double degeneracies found for the IFEM is characteristic in general of one-dimensional systems of particles interacting by singular potentials. For example, we have solved the problem of two Coulomb particles bound in a harmonic potential and find the same double degeneracies arising. By arguments similar to those of Sec. II.A we can show for the general case of an arbitrary binding (stationary) potential that if the energy is to be finite, the wavefunctions must vanish at least as rapidly as X_2 near $X_2=0$. Hence, the *general* solutions in the region $X_2>0$ and $X_2<0$ can be joined to form either symmetric or antisymmetric wavefunctions by satisfying the appropriate boundary conditions. An interesting corollary to this result is that for one-dimensional systems of two fermions interacting by singular potentials, $S=0$ and $S=1$ states are degenerate, a conclusion in accord with Lieb and Mattis'[25] result: "If $S>S'$, then $E(S)>E(S')$ unless V is pathologic, in which case $E(S)\geq E(S')$," where $E(S)$ is the ground-state energy. The Coulomb potential is an example of a pathologic potential.

The pathological nature of the 1-D Coulomb potential has certainly "distorted" physics, since we know that in three-dimensional systems of two fermions, the $S=0$ state is of lower energy than the $S=1$ state. The Coulomb potential is too "strong" in one dimension. Hence, in order to apply our model to real systems, some modifications, or at least conventions, will have to be made. For example, our treatment above of the IFEM suggests at least two ways of handling the pi-electron system of linear conjugated molecules. One way is to expand a trial wavefunction as a linear combination of hard-sphere eigenfunctions and use the Ritz method to find the approximate eigenvalues and functions. This does not get rid of the degeneracy, but at least allows us to calculate the integrals in the Hamiltonian matrix. An alternative method is to assume that the electrons move on parallel lines so that the Coulomb potential $1/|x_{ij}|$ is replaced by $1/(d^2+x_{ij}^2)^{1/2}$, where d is distance between the lines. It has been suggested that this modified potential corresponds to a 2-D average over a 3-D Coulomb potential.[26] The latter method has the advantage of no degeneracy, but the disadvantage that d cannot be known *a priori*.

The results of this investigation are quite encouraging. We have seen that the finite-difference method gives accurate eigenvalues and functions of a model Hamiltonian. Although we have been concerned primarily with the solution of a specific quantum-mechanical problem, further work now in progress demonstrates its general applicability in the solution of one- and two-dimensional Schrödinger equations involving both singular stationary (nuclear) potentials and inter-

[25] E. Lieb and D. Mattis, Phys. Rev. **125**, 146 (1962).

[26] E. E. Nikitin, *Methods of Quantum Chemistry* (Academic Press Inc., New York, 1965).

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TABLE VI. Coefficients of hard-sphere eigenfunctions in expansions of various approximate ground-state wavefunctions for the 4.00-a.u. well.

Approximation	Coefficients										
	C_{12}	C_{13}[a]	C_{14}	C_{15}[a]	C_{23}	C_{24}[a]	C_{25}	C_{34}	C_{35}[a]	C_{45}
Finite difference ($M=78$)	0.991	2.06×10^{-6}	3.67×10^{-2}	1.04×10^{-6}	-0.124	7.70×10^{-7}	7.24×10^{-3}	-2.62×10^{-2}	2.86×10^{-8}	-1.01×10^{-2}
HSM	1.000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
HSM perturbation treatment	1.000	-1.49×10^{-5}	3.57×10^{-2}	-7.61×10^{-6}	-0.135	-5.87×10^{-7}	1.00×10^{-2}	-3.72×10^{-2}	1.74×10^{-6}	-1.56×10^{-2}
HSM variational treatment (10 functions)	0.991	-1.44×10^{-5}	3.48×10^{-2}	-6.97×10^{-6}	-0.123	1.41×10^{-6}	7.32×10^{-3}	-2.64×10^{-2}	1.91×10^{-6}	-1.05×10^{-2}

[a] These coefficients should vanish by group theory.

particle potentials. By employing finer meshes (diagonalizing larger matrices) we can obtain accurate approximations to the lower excited states of chemically important systems such as the helium atom. The bound states of many "unbounded" problems, e.g., two electrons in a harmonic well, the quartic oscillator, pose no difficulty since the boundary conditions at infinity may be imposed at finite values of the arguments which are sufficiently large to insure that the wavefunction is very small by comparison to its maximum value. Finally we note that systems of coupled differential equations may be treated by the FD method, e.g., the Hartree–Fock equations.

ACKNOWLEDGMENTS

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APPENDIX

The first-order correction to the energy of hard-sphere state $\phi_{\mathrm{HSM}}(n, m)$ is given by

$$E_{nm}^{(1)}=I=\int_0^a dx_1'\int_0^{x_1'} dx_2'\phi^{+}_{\mathrm{HSM}}(n, m; x_1', x_2') \times|x_1'-x_2'|^{-1}\phi^{+}_{\mathrm{HSM}}(n, m; x_1', x_2'), \quad \text{(A1)}$$

since the integrand is symmetric with respect to $\mathbf{R}_1$ and ϕ^{+}_{HSM} is normalized over the *half*-square. Making the changes of variables

$$x=\pi x_1'/a, \qquad y=\pi x_2'/a, \quad \text{(A2a)}$$

and

$$\bar{x}=\tfrac{1}{2}(x+y), \qquad \bar{y}=(x-y), \quad \text{(A2b)}$$

we obtain from Eq. (A1)

$$I=(4)\frac{2}{a}\frac{2}{\pi}\int_0^{\pi} d\bar{y}\int_{\bar{y}/2}^{\pi/2} \times d\bar{x}\{\sin[\tfrac{1}{2}n(2\bar{x}+\bar{y})]\sin[\tfrac{1}{2}m(2\bar{x}-\bar{y})] -\sin[\tfrac{1}{2}m(2\bar{x}+\bar{y})]\sin[\tfrac{1}{2}n(2\bar{x}-\bar{y})]\}^2\bar{y}^{-1}. \quad \text{(A3)}$$

Hence we see that $E_{nm}^{(1)}$ is proportional to $1/a$, the reciprocal of the well width. The integrand in Eq. (A3) is expanded to obtain a sum of three terms, each term consisting of a product of four sines of arguments involving the sum of $\bar{x}$ and $\bar{y}$. These three terms may be further broken down by trigonometric identities into sums of products of sines and cosines. Thus

$$I=\frac{8}{a}\frac{2}{\pi}\int_0^{\pi} d\bar{y}\int_{\bar{y}/2}^{\pi/2} d\bar{x}(\bar{I}_1+\bar{I}_2+\bar{I}_3), \quad \text{(A4a)}$$

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where

$$\begin{aligned}\bar{I}_1(n,m)=&\tfrac{1}{4}\bar{y}^{-1}\{1-\cos n\bar{y}\cos 2n\bar{x}+\sin n\bar{y}\sin 2n\bar{x}\\&-\cos m\bar{y}\cos 2m\bar{x}-\sin m\bar{y}\sin 2m\bar{x}\\&+\tfrac{1}{2}\cos(n-m)\bar{y}\cos 2(n+m)\bar{x}\\&-\tfrac{1}{2}\sin(n-m)\bar{y}\sin 2(n+m)\bar{x}\\&+\tfrac{1}{2}\cos(n+m)\bar{y}\cos 2(n-m)\bar{x}\\&-\tfrac{1}{2}\sin(n+m)\bar{y}\sin 2(n-m)\bar{x}\}\end{aligned}$$

$$\begin{aligned}\bar{I}_2(n,m)=&-\tfrac{1}{2}\bar{y}^{-1}\{\cos 2n\bar{x}\cos 2m\bar{x}-\cos m\bar{y}\cos 2n\bar{x}\\&-\cos n\bar{y}\cos 2m\bar{x}+\cos n\bar{y}\cos m\bar{y}\}\end{aligned}\tag{A4b}$$

$$\bar{I}_3(n,m)=\bar{I}_1(m,n).$$

Carrying out the integrations over $\bar{x}$, we have

$$\begin{aligned}I=\frac{8}{a}\frac{1}{2\pi}\int_0^{\pi}d\bar{y}\Bigg\{&\pi\left[\frac{\tfrac{1}{2}-\tfrac{1}{2}\cos(n+m)\bar{y}}{\bar{y}}\right]\\&+\pi\left[\frac{\tfrac{1}{2}-\tfrac{1}{2}\cos(n-m)\bar{y}}{\bar{y}}\right]\\&-1+\{(2n)^{-1}-[4(n+m)]^{-1}-[4(n-m)]^{-1}\}\frac{\sin 2n\bar{y}}{\bar{y}}\\&+\{(2m)^{-1}-[4(n+m)]^{-1}+[4(n-m)]^{-1}\}\frac{\sin 2m\bar{y}}{\bar{y}}\\&+\{[2(n+m)]^{-1}-(2n)^{-1}-(2m)^{-1}\}\frac{\sin(n+m)\bar{y}}{\bar{y}}\\&+\{[2(n-m)]^{-1}-(2n)^{-1}+(2m)^{-1}\}\frac{\sin(n-m)\bar{y}}{\bar{y}}\\&+\cos n\bar{y}\cos m\bar{y}\Bigg\}.\end{aligned}\tag{A5}$$

The first two terms of Eq. (A5) may be written in the form

$$\int_0^{\alpha}\frac{\sin^2 x}{x}\,dx=\tfrac{1}{2}[\ln\gamma+\ln\alpha-\mathrm{Ci}(2\alpha)],\tag{A6}$$

where γ is Euler's constant and Ci is the cosine integral.[27] The last term of Eq. (A5) vanishes since $n\neq m$. Thus we obtain finally

$$\begin{aligned}I=(4/\pi a)\,(&\tfrac{1}{2}\pi\{\ln\gamma+\ln\tfrac{1}{2}[(n+m)\pi]-\mathrm{Ci}(n+m)\pi\}\\&+\tfrac{1}{2}\pi\{\ln\gamma+\ln\tfrac{1}{2}[(n-m)\pi]-\mathrm{Ci}(n-m)\pi\}-\pi\\&+\{(2n)^{-1}-[4(n+m)]^{-1}-[4(n-m)]^{-1}\}\,\mathrm{Si}(2n\pi)\\&+\{(2m)^{-1}-[4(n+m)]^{-1}+[4(n-m)]^{-1}\}\,\mathrm{Si}(2m\pi)\\&+\{[2(n+m)]^{-1}-(2n)^{-1}-(2m)^{-1}\}\,\mathrm{Si}(n+m)\pi\\&+\{[2(n-m)]^{-1}-(2n)^{-1}+(2m)^{-1}\}\,\mathrm{Si}(n-m)\pi),\end{aligned}\tag{A7}$$

where Si is the sine integral.

[27] W. Gröbner and N. Hofreiter, *Integraltafel* (Springer-Verlag, Vienna, 1961), p. 129.

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